



Importance of binder compositions to the dispersion and electrochemical properties of water-based LiCoO₂ cathodes

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HIGHLIGHTS

- Increasing [SBR] of SBR/CMC binder blend uniforms binder distribution in cathodes.
- Increasing [SBR] of SBR/CMC causes higher agglomeration of active powders.
- Binder uniformity rather than the powder dispersion dominates the cell performance.

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ABSTRACT

The effects of the styrene–butadiene rubber (SBR) to sodium carboxymethyl cellulose (CMC) blending ratio of the water-based SBR/CMC binder on the dispersion and the physical and electrochemical properties of LiCoO₂ electrodes are studied. Based on the results of dispersion analyses, it is determined that CMC is efficient in dispersing LiCoO₂, and the dispersion of the LiCoO₂ electrode slurry becomes better when the fraction of SBR in the binder is decreased. Based on physical and electrochemical measurements, however, decreasing the SBR fraction makes the distribution of the binder in the dried electrode sheet less uniform, which results in decreased adhesion strength and increased surface resistance of the electrode sheets. In addition, this study reveals that the binder distribution has a greater influence on the electrical and electrochemical properties of the LiCoO₂ electrodes than the dispersion of cathode powders has.

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1. Introduction

To make electrode sheets for lithium-ion (Li-ion) cathodes or anodes with appropriate mechanical properties, such as tensile strength, toughness and compressibility, the electrode-active material and conductive agent generally have to be blended with specific polymeric binders [1–3]. To mix the electrode-active material and the conductive agent homogeneously with polymeric binder, appropriate solvent that can dissolve the binder is required. According to the type of solvent used, the as-prepared electrode slurry can be classified as two systems – a water-based (aqueous) system and an organic solvent-based (non-aqueous) system. For environmental consistency and cost considerations, the water-based system, which uses environmentally benign binders and solvents, has attracted increasing attention and has become

a new trend in the manufacture of Li-ion electrodes [4–7]. Among water-compatible polymers, the aqueous emulsion of styrene–butadiene rubber (SBR) blended with water-soluble sodium carboxymethyl cellulose (CMC) is the commonly used binder for anodes [8–12] and cathodes [13–17] of Li-ion batteries. It is known that SBR provides not only good binding for electrode powders but also the required adhesion of electrode sheets to the current collector. Nevertheless, SBR comes in the form of an aqueous emulsion, which has very low viscosity and, therefore, does not facilitate the wetting of its fabricated electrode slurry on the current collector during casting. To improve the wetting, SBR is generally blended with the thickening agent CMC. CMC has a strong shear-thinning behavior that adjusts the slurry rheology. According to literature [6,8,10,14–16,18–20], the needed amount of this binder blend (SBR/CMC) is usually in the range of 1–5% based on the weight of the electrode sheet. For the adjustments of the rheology and adhesion properties, the relative ratio of SBR to CMC is not constant, but is commonly set to 1:1 or confined to the range from 5:1 to 3:7.

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On the other hand, it has also been reported that CMC exhibits dispersion efficiency for most electrode actives and conductive graphites [6,8,20]; i.e., CMC can improve the dispersion of electrode materials in addition to its function of modifying the rheology for electrode casting. Since CMC can disperse the electrode powders (electrode active and conductive agent), the relative ratio of SBR to CMC in the binder blend becomes essential and must be considered because the ratio may affect the dispersion property of the electrode slurries. However, most investigations regarding the dispersion of water-based electrode slurries by using SBR/CMC as the binder merely focus on the study of the effects of the substitution degree (DS) and the molecular weight of CMC. The importance of the relative ratio of SBR to CMC for the dispersion, and the physical and electrochemical properties is neglected. Moreover, our previous investigation revealed that the polymeric binder would migrate with the solvent during the drying process of the electrode sheet [21], resulting in a non-uniform distribution of the binder in the electrode, and also that the migrated amount of binder correlates closely with the amount of the binder adsorbed on the electrode powders. SBR and CMC have different chemical natures; thus, it is normal that they exhibit different interactions with the electrode powders and have different adsorption amounts. Therefore, when two SBR/CMC binders have different relative ratios of SBR to CMC, it is reasonable that the electrode powders adsorb different amounts of the binders and it is possible to have different degrees of uniformity of binder distribution in the dried electrode sheet. The uniformity of binder distribution in a dried electrode sheet is important because it usually dominates the binding strengths of the electrode powders and the adhesion strength between the electrode sheet and the current collector, which will determine the electrochemical performance of the electrodes.

In this investigation, we keep the concentration of the SBR/CMC binder blend constant and change the relative ratio of SBR and CMC to study its effects on the dispersion and the distribution uniformities of the electrode powders and binders, in which the used electrode active material was LiCoO_2 whose electrochemistry is well known. Moreover, the importance of the dispersion of the cathode powders and the uniformity of the binder distribution in the dried electrode sheet for the physical and electrochemical performance of water-based electrodes are also examined. Based on these analyses, it is clear that the dispersion of the cathode powders and the uniformity of the binder distribution are very sensitive to the relative ratio of SBR and CMC of the binder, and that their blending ratio determines the eventual electrical and electrochemical properties of the electrodes. It was also found that the ratio of 1:1 that is commonly used in most studies may not be optimal.

2. Experimental

The cathode-active material used in this study was a high-purity LiCoO_2 powder (L106, LICO, Taiwan). The powder had a median size of $8.0\ \mu\text{m}$ with a standard deviation of $0.45\ \mu\text{m}$ measured by the light scattering (LS-230, Coulter Counter, USA) method. Synthetic graphite (Timrex KS-6, Timcal A+G Sins, Switzerland) with a d_{90} of $5.8\text{--}7.1\ \mu\text{m}$ was used as a conductive agent. Commercially available SBR (Asahi Kasei Corporation, Japan) in the form of an aqueous emulsion of 15 wt% with a viscosity of $130\ \text{mPa}\cdot\text{s}$ at $25\ ^\circ\text{C}$ was used as the binder. CMC (Aldrich, USA) was used as a thickening agent for the SBR with an average molecular weight of $250,000\ \text{g}\cdot\text{mol}^{-1}$ and a degree of substitution of 1.2. De-ionized water was used as the solvent for preparing the aqueous electrode slurries.

The surface chemistry of LiCoO_2 was characterized by the technique known as the electroacoustic method (ZetaProbe,

Colloidal Dynamics Inc., USA). To measure zeta potentials, aqueous suspensions with a solid loading of 5 wt% LiCoO_2 were prepared in the absence and presence of SBR or CMC. The pH values of the suspensions were adjusted by aqueous solutions of hydrochloric acid and sodium hydroxide. The dispersion properties of the electrode slurries were analyzed by using a rotational rheometer (AR1000, TA Instruments Ltd., UK). For rheological measurements, aqueous electrode slurries with 68.0 wt% LiCoO_2 powder were prepared by mixing additives of 6.1 wt% KS-6 and 1.6 wt% binder blend of SBR and CMC, which were mingled with various ratios. Note that the solid loading of LiCoO_2 was based upon the weight of the de-ionized water and the contents of all additives were based on the LiCoO_2 powder. The slurries were de-agglomerated and mixed by ball milling with Y_2O_3 -stabilized ZrO_2 media for 3 days at room temperature. For the measurements of the adsorptions of binder blend on the electrode powders, the as-prepared electrode slurry was centrifuged at a speed of 5500 rpm for 30 min to separate the supernatants from the powders. The concentration of the binder blend adsorbed on the powders was determined by thermogravimetric analysis (TGA) (Q50, TA Instruments Ltd., UK) at a heating rate of $10\ ^\circ\text{C}\cdot\text{min}^{-1}$ from $25\ ^\circ\text{C}$ to $800\ ^\circ\text{C}$ in air.

For analyzing the binder distribution in a dried electrode sheet, the as-prepared electrode slurry was cast in an aluminum dish, which had a thickness of approximately $1500\ \mu\text{m}$ after drying at $80\ ^\circ\text{C}$. The dried electrode sheets were then stored in a dry box with a $25\ ^\circ\text{C}$ controlled temperature and a 50% relative humidity. The binder content inside the sheets was determined by TGA at a heating rate of $10\ ^\circ\text{C}\cdot\text{min}^{-1}$ from room temperature to $800\ ^\circ\text{C}$ in air. Samples for TGA were prepared by removing powders from the electrode sheets with a sharp tungsten carbide–cobalt knife. Note that the powder samples that were removed before the TGA measurements were also stored in the dry box with a controlled environment, as stated earlier.

On the other hand, the electrode slurries were also cast on one side of an aluminum (Al) foil by using a bench-type tape caster, and the thickness of the sheets was approximately $80\ \mu\text{m}$ after drying at $80\ ^\circ\text{C}$. Each dried sheet has to be further dried in a vacuum oven under a pressure of 10^{-3} Torr and a temperature of $100\ ^\circ\text{C}$ for another 24 h before the physical and electrochemical properties can be measured. To compress the electrode sheets, a pressure of $7.5\ \text{tons}\cdot\text{cm}^{-2}$ was applied. The microstructures of the compressed and uncompressed electrode sheets were examined using a field emission scanning electron microscope (FESEM, S-470, Hitachi, Japan). The surface resistance of each electrode sheet was measured with a two-point resistance test using a MCP-TESTER FP analyzer. The adhesion strength of the uncompressed cathode sheets on the Al substrate was measured by a force gauge (JSV-500D, Algol, Taiwan). The electrochemical performance was evaluated by assembling cathode-limited 2016 lithium coin cells. The LiCoO_2 electrode was used for the cathode. A lithium metal foil electrode was used as the anode. A separator (Celgard 2500) was placed between the cathode and the anode. The electrolyte was 1.0 M lithium hexafluorophosphate (LiPF_6 , Ferro Corp., Cleveland, OH, USA) in EC:PC:DEC (3:2:5 in volume) mixed solvents. The rate capability was tested by charging the cells to 4.2 V at a constant current of 0.2 C and then discharging to 2.75 V at 0.2 C.

3. Results and discussion

3.1. Dispersion of electrode slurry

Fig. 1 shows the effect of adding the organic additives, SBR and CMC, on the surface chemistry of LiCoO_2 . The isoelectric point (IEP) of LiCoO_2 was not observed, and all its zeta potentials were approximately zero in the investigated pH range, indicating that

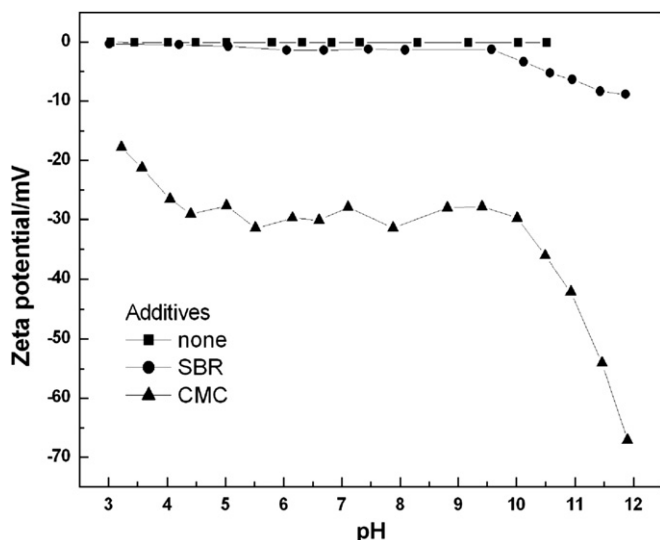


Fig. 1. Zeta-potentials of 5 wt% LiCoO₂ in de-ionized water with the additives of (a) none, (b) 1.6 wt% SBR, and (c) 1.6 wt% CMC. The concentrations of additives are based upon the weight of LiCoO₂.

the used LiCoO₂ is quite insensitive to protons (H⁺) and hydroxyl anions (OH⁻). An insignificant shift of the zeta potential curve of LiCoO₂ was obtained when SBR was added. Nevertheless, the addition of CMC shifts the zeta potentials of LiCoO₂ in the negative direction, demonstrating the occurrence of specific adsorption of CMC on LiCoO₂. Because CMC can dissociate to carry anionic charges in an aqueous solution, the specific adsorption of CMC increases the negative charge density and the magnitude of the zeta potentials of LiCoO₂, which can provide the electrostatic or electrosteric stabilization mechanism for the dispersion of LiCoO₂ in the aqueous suspension. On the other hand, the addition of SBR is definitely inefficient in the dispersion of LiCoO₂.

Fig. 2(a) shows the apparent viscosity as a function of shear rate for the aqueous LiCoO₂ slurries in the presence of a binder blend of SBR and CMC mingled in various relative weight ratios. By adding the binder blend containing 90% and 70% SBR, both slurries demonstrate the complex rheology of shear-thinning at low shear rate and shear-thickening at high shear rate. As the fraction of SBR in the SBR/CMC binder ([SBR]) is decreased, the viscosity of slurries increases and the flow behavior tends to be more shear-thinning. However, the increasing viscosity with decreasing [SBR] does not

indicate that lower [SBR] will lead to poorer dispersion of electrode powders because the increase of viscosity might be caused by the exhibition of a higher ratio of high-viscous CMC. To clarify the exact effect of [SBR] on the dispersion of electrode powders, the result of the relative viscosity (η_r) as a function of shear rate was shown in Fig. 2(b), in which the rheological contribution from the rheological nature of the SBR/CMC binder was excluded. On the contrary, it was found that the relative viscosity decreases with decreasing [SBR], revealing that the dispersion of electrode powders is facilitated by the use of lower [SBR]. Nevertheless, the slurries containing binder with 90% and 70% [SBR] retain the same complex rheology as those shown in Fig. 2(a). This complex rheology (i.e., shear-thinning shown at low shear rate and shear-thickening shown at high shear rate) suggests that the electrode powders in the slurries exhibited in soft agglomerates and aggregates (hard agglomerates) simultaneously. The soft agglomerates can easily be broken up when applying a simple shear stress, whereas the aggregates cannot. For the slurry containing binder with 50% [SBR], only shear-thickening was observed, suggesting the presence of hard aggregates in the slurry. For the slurries containing binders with 30% and 10% [SBR], both have the flow behavior of a Newtonian fluid, indicating the electrode powders are well dispersed with absence of agglomerates or aggregates.

In addition to the analyses of rheology, the effect of [SBR] on the dispersion of electrode powders in slurries was also assessed by measuring the porosity of the dried LiCoO₂ electrode sheets. When the powders inside the electrode sheet are agglomerated, they will be less compacted and presenting a lower relative density and higher porosity. The porosities of compressed (ϕ_p) and uncompressed (ϕ) LiCoO₂ electrode sheets as a function of [SBR] are shown in Fig. 3. By decreasing the [SBR], for which the dispersions of electrode powders become better, the porosities decrease significantly from 74% to 45% for the uncompressed electrode sheets and from 50% to 15% for the compressed ones. The very high porosities of the uncompressed electrode sheets might be because the slurries were not de-foamed before casting, and thus the pinholes contained in the dried sheets also contributed to the porosity. Nevertheless, the significant decreasing trend of porosity with [SBR] still evidences the benefit of decreasing [SBR] for the dispersion of aqueous LiCoO₂ slurries.

3.2. Binder distribution and electrode adhesion

Although decreasing [SBR] is beneficial to the dispersion of electrode powders, SBR is important and a certain amount is

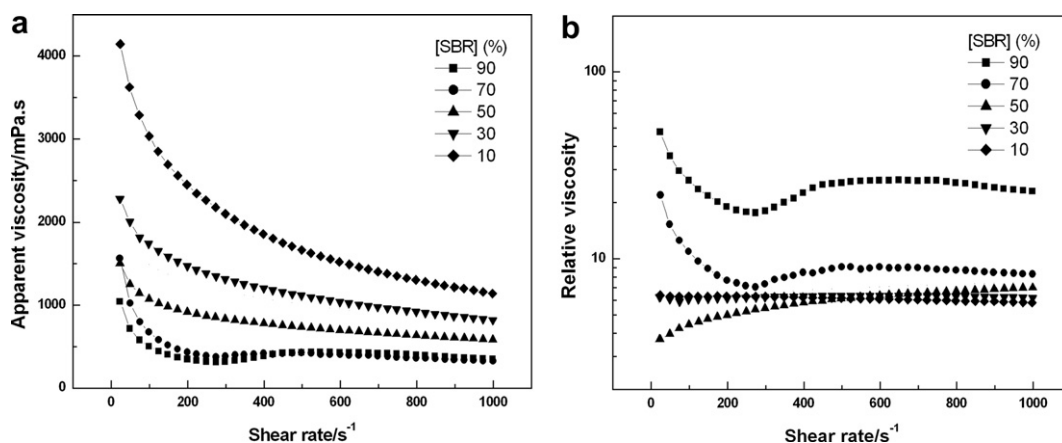


Fig. 2. (a) Apparent viscosity as a function of shear rate for 68 wt% aqueous LiCoO₂ slurries with additions of binders with various [SBR]. (b) Relative viscosity as a function of shear rate for 68 wt% aqueous LiCoO₂ slurries with additions of binders with various [SBR].

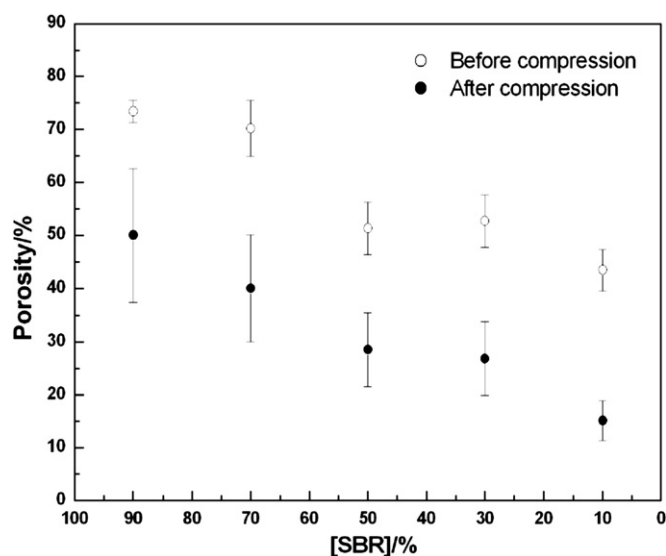


Fig. 3. Porosity of electrode sheets as a function of [SBR].

required to provide the binding strength of electrode sheets. Fig. 4 shows the adhesion strengths of compressed and uncompressed electrode sheets, γ_p and γ , as a function of [SBR]. Without being compressed, the electrode sheets exhibit adhesion strengths higher than 100 g cm^{-1} at [SBR] greater than 70%. In addition to the higher fraction of SBR, the more uniform distribution of binder in the electrode sheet with [SBR] greater than 70% may also cause the stronger adhesion for electrodes. Fig. 5 shows the experimental contents of binder as a function of [SBR] at the depths of 5%, 50%, and 95% from the bottom side of the electrode sheet. The theoretical contents of the binder were also compared in this figure, which were calculated on the basis of migration-controlled kinetics that has been detailed in a previous investigation [21]. To magnify the effect of [SBR] on the distribution of binder, the thickness of the dried electrode sheets used in Fig. 5 is $1500 \mu\text{m}$. It is obvious that the experimental results correspond well with the theoretical calculations. By decreasing the [SBR], the difference between the binder contents at the top (95%) and bottom (5%) sides ($\Delta\chi$) increases; i.e., the binder is less uniformly distributed and stays insufficient at the

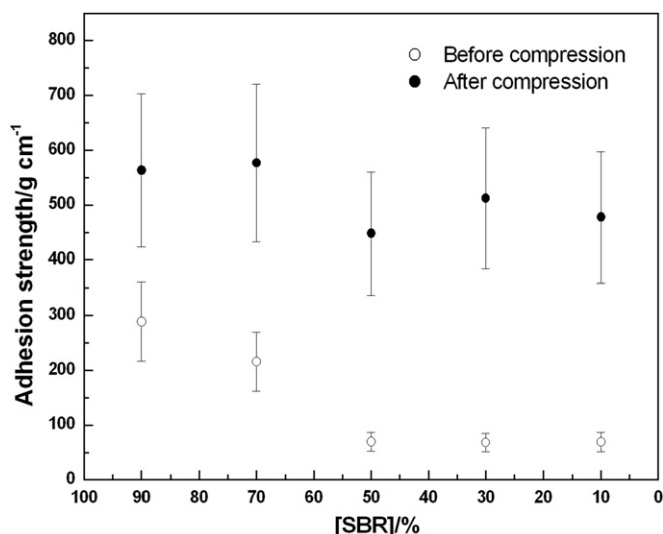


Fig. 4. Adhesion strength of electrode sheets as a function of [SBR].

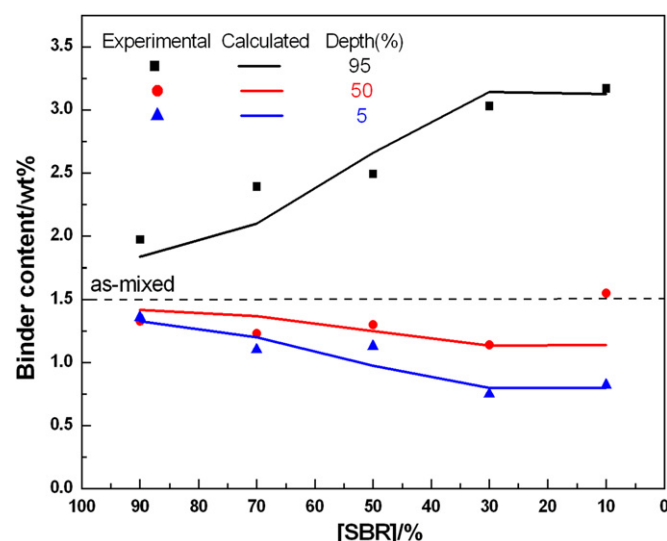


Fig. 5. Experimentally measured and calculated binder contents at various depths from the bottom side of electrode sheets as a function of [SBR]. The thickness of electrode sheets is $1500 \mu\text{m}$.

bottom side of the electrode sheet when the [SBR] is decreased. Moreover, based on theoretical considerations and calculations, it is understood that the different uniformities of the binder distributions at different [SBR] is primarily attributed to the different amounts of binder adsorbed on powders. By decreasing [SBR] from 90%, 70%, 50%, 30% to 10%, the adsorptions of binders (Q) decrease, respectively, from 1.15%, 1.06%, 0.86%, 0.76% to 0.65% based on the weights of the electrode powders. The lesser adsorption leads to a greater migration and a lesser uniform distribution of the binder. This decreasing trend of binder uniformity corresponds well to the decrease of electrode adhesion; i.e., the poorer adhesion at lower [SBR] is attributed to the lesser uniformity of the binder distribution in the electrode sheet. On the other hand, Fig. 4 also shows that the adhesion strengths are significantly increased when the electrode sheets are compressed. The adhesion strengths become approximately good in the range of $400\text{--}500 \text{ g cm}^{-1}$ after compression. It is though that the compression process may have changed the binder distribution in the electrode sheet.

In addition to the binder, migration of the conductive graphite also occurred and was correlated to the [SBR]. Fig. 6 reveals the top microstructures of the as-cast electrode sheets containing binders with 90% and 10% [SBR]. An apparent accumulation of graphite was observed on the top surface of the electrode sheet when [SBR] is 90% (Fig. 6(a)), which was not observed for that corresponding to [SBR] of 10% (Fig. 6(b)). The effect of [SBR] on the uniformity of the graphite distribution is opposite to its effect on the uniformity of the binder distribution. This could be because the binder is dissolved in a solvent and thus its re-distribution is under the domination of solvent migration. Accompanying the evaporation of the solvent from the top surface of the drying electrode sheet, the dissolved free binder migrates upward. With the decrease of [SBR], the amount of non-adsorbed binder increases and hence the migration of the binder increases. However, graphite is merely suspended and its re-distribution primarily correlates to the rheology of slurries [21]. Since the slurry has a lower apparent viscosity at higher [SBR] (Fig. 2(a)), it should be easier for the "light" graphite to flow upward in the slurry containing binder with 90% [SBR] than in that with 10% [SBR].

Based on the above results, the physical properties of the as-prepared slurry and electrode sheet at various [SBR] were also revealed and compared in Table 1 for the clarity of the effect of

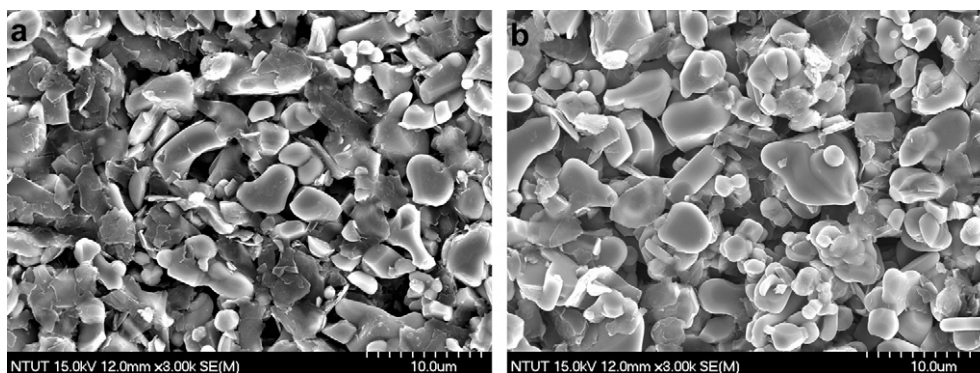


Fig. 6. SEM images of the top surfaces of the as-cast electrode sheets after drying. Panels (a) and (b) are the electrode sheets at [SBR] of 90% and 10%, respectively.

[SBR]. It is clear that decreasing the [SBR] of the binder blend results in the disadvantages of a lesser uniform distribution of binder and a poorer adhesion of the electrode sheet although it also leads to the advantage of a better dispersion of the electrode powders. In the following, the effects of [SBR] on the electrical resistance and capacity of the LiCoO₂ electrodes are investigated to clarify whether the binder uniformity or the powder dispersion dominates the electrochemical performances of the as-prepared LiCoO₂ electrodes.

3.3. Electrical and electrochemical properties

Fig. 7 shows the surface resistances of the electrode sheets with and without compression as a function of [SBR]. When the electrode sheets are not compressed, it is obvious that the surface resistance increases with decreasing [SBR], demonstrating the detriment of decreasing [SBR] for the electronic conduction. Although the electrode powders are better dispersed in the electrode sheet when [SBR] is lower, the adhesion of electrode sheets to the current collector is poorer due to the depletion of binder at the bottom side (Figs. 4 and 5), which is harmful to the electronic conduction. On the contrary, the electrode sheets have a decrease of surface resistance with decreasing [SBR] when they are compressed. This opposite result to that of the uncompressed electrode sheets suggests that the electronic conduction of the compressed electrode sheets is not under the domination of the binder distribution or the electrode adhesion but may be dominated by the dispersion of electrode powders because the adhesions have become approximately sufficient after compression. Although the extension force of compression may break up some agglomerates and alter the dispersion of electrode powders. Only

the agglomerates in the electrode sheets containing binders with 90% and 70% [SBR] can be broken up due to the compression, and the hard aggregates still remain in the electrode sheets with 90%, 70%, and 50% [SBR]. Therefore, it is believed that the increasing trend of the dispersion of electrode powders with the decrease of [SBR] is unchanged even after compression and determines the electrical property of the electrode sheets. As a result, it is known that the electrical property is under the domination of the powder dispersion when the electrode sheets are compressed; otherwise, the binder distribution as well as the electrode adhesion has higher priority than the powder dispersion to determine the electrical property of the electrodes.

The effect of [SBR] on the electrochemical properties of cells was studied further. Fig. 8(a) shows the discharge curves at 0.2 C for the cells with uncompressed LiCoO₂ electrodes. It was observed that the capacities decrease from 111.3 mAh g⁻¹ at 90% [SBR], 103.9 mAh g⁻¹ at 70% [SBR] to 93.2 mAh g⁻¹ at 50% [SBR]. This decreasing trend of the capacity with the decrease of [SBR] corresponds to the result of Fig. 7, which demonstrates the increase of the surface resistance with the decrease of [SBR]. That is, the decreased capacity with the decrease of [SBR] is caused by the increase of surface resistance that is due to the poorer uniformity of binder and adhesion of the electrode. Nevertheless, the capacities of the cells with electrodes with 30% and 10% [SBR] are not continuing to decrease but increase to 113.9 and 107.4 mAh g⁻¹, respectively. It is believed that the better capacities of these two

Table 1

Physical properties including the adsorption of binders on powders (Δ), relative viscosity (η_r from Fig. 2(b)), binder distribution ($\Delta\chi$ from Fig. 5), porosity (ϕ and ϕ_p from Fig. 3) and adhesion strength (γ and γ_p from Fig. 4) for slurries and electrodes prepared at various weight fraction of SBR ([SBR]).

[SBR] (%)	Ω (%)	Rheological behavior	$\Delta\chi$ (%)	ϕ/ϕ_p (%)	γ/γ_p (g cm ⁻¹)
		η_r at 1000 s ⁻¹			
90	1.15	Shear-thinning/-thickening 23.0	0.61	73.4/50.0	288.3/563.3
70	1.06	Shear-thinning/-thickening 8.3	1.29	70.2/40.0	215.8/576.7
50	0.86	Shear-thickening 7.0	1.36	51.3/28.6	69.4/448.3
30	0.76	Newtonian 6.2	2.28	52.7/26.8	68.1/512.5
10	0.65	Newtonian 5.8	2.35	43.4/15.1	69.2/477.8

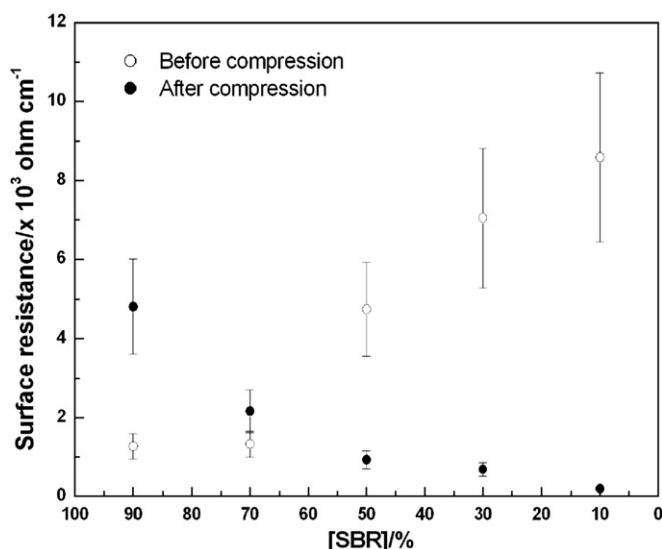


Fig. 7. Surface resistance of electrode sheets as a function of [SBR].

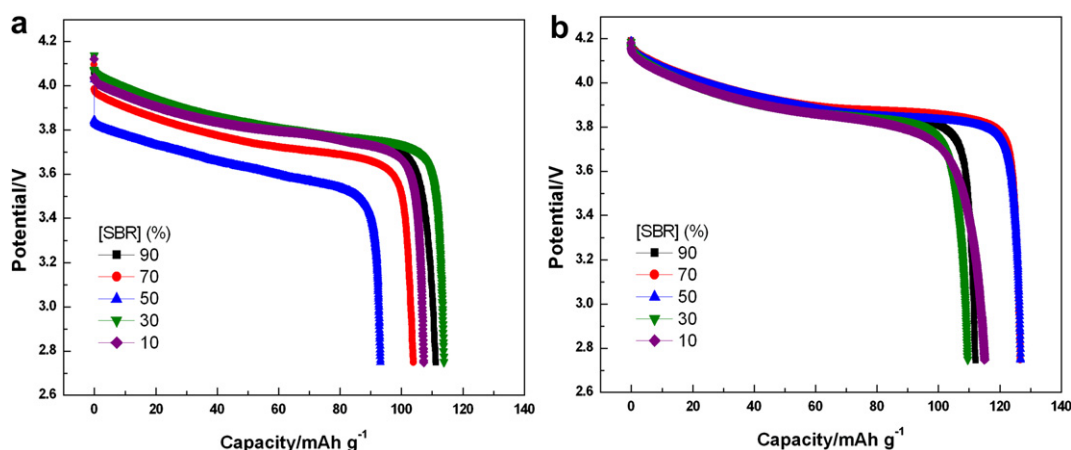


Fig. 8. Charge-discharge profiles at the charge and discharge rate of 0.2 C for (a) uncompressed and (b) compressed electrode sheets as a function of [SBR].

electrodes should be attributed to their excellent dispersion of electrode powders. As shown in Fig. 2(b) the slurries containing binders with 30% and 10% [SBR] have Newtonian rheology, which the electrode powders are well dispersed in the absence of agglomerates or aggregates. Hence, the much better contact between the active LiCoO₂ and the conductive graphite can very well reduce the IR-drop of the electrode sheets and improve the capacities.

For the cells with compressed electrodes, approximate plateau voltages with different specific discharge capacities were obtained (Fig. 8(b)). The result of the approximate plateau voltages indicates that the IR-drops for these electrodes are similar because of their approximately sufficient adhesions (Fig. 4). Besides, capacities of cells with electrodes containing binders with 90%, 30% and 10% [SBR] were found that were significantly poorer than the capacities of cells with 70% and 50% [SBR]. Because we know that the electrical property of the compressed electrode sheet is primarily determined by the dispersion of electrode powders, it is clear the electrode sheet containing binder with [SBR] of 90% has poor capacity. The electrode sheets containing binders with 30% and 10% [SBR] have the best dispersions of electrode powders; however, they showed poorer capacities of about 109.6–115.1 mAh g⁻¹, which is lower than the capacities of 126.7 mAh g⁻¹ for the electrodes containing binders with 70% and 50% [SBR]. According to Ref. [22], the porosity of the electrode sheets is a key factor in affecting the electrochemical performances. That is, having an appropriate porosity is essential to have good electrochemical properties for the electrode sheets because a too low porosity of more dense electrodes restricts the lithium-ion diffusion and a too high porosity of less dense electrodes limits the electronic conductivity. Therefore, the result of the higher capacities of the electrode sheets containing binders with 70% and 50% [SBR] can very possibly be attributed to their porosities of 40% and 29% (Fig. 3) that are the closest ones to the suggested optimum of 30–35% [22].

4. Conclusions

In this investigation, we revealed the importance of the blending ratio of SBR to CMC of the SBR/CMC binder on the dispersion, and the physical and electrochemical properties of water-based LiCoO₂ electrode sheets. Because CMC is dissociable, its adsorbed LiCoO₂ is able to carry sufficient charge density in the aqueous slurry and can be well dispersed based on the electrostatic or the electrosteric stabilization mechanism. Moreover, it was found that decreasing the [SBR] of the binder is beneficial to the

dispersion of the LiCoO₂ electrode slurry. However, the amount of the SBR/CMC binder adsorbed on the electrode powders decreases with decreasing [SBR], leaving a greater amount of free binder that can migrate with water up to the top surface of the electrode sheet during the drying process in the aqueous suspension. Hence, the distribution of binder in the dried electrode sheet is of lesser uniformity and the resulting adhesion property is poor when [SBR] is lower. On the other hand, conductive graphite will also redistribute during drying. Because of its low density, graphite can migrate in the low-viscous slurry. As a result, the re-distribution of graphite in the electrode slurry containing the binder with higher [SBR], which has lower apparent viscosity, is more significant; i.e., a lesser uniform distribution of graphite in the dried electrode sheet is obtained when [SBR] is higher. In the measurements of the electrical property, it was found that the surface resistance of the electrode sheet is primarily dominated by the properties of the binder distribution and electrode adhesion but not the dispersion of electrode powders except when the electrode sheets are compressed. Therefore, when the [SBR] is decreased, the surface resistance of the uncompressed electrode sheet increases although the dispersion of the electrode powders has become better. In the measurements of the electrochemical properties, it was found that the uncompressed electrodes also showed a decreasing trend of capacity with the decrease of adhesion strength, except for those with 30% and 10% [SBR] because of their excellent dispersions of electrode powders. On the other hand, the electrodes with 70% and 50% [SBR] that have the lowest capacities before being compressed have conversely the highest capacities when they are compressed, which should be correlated to their exhibition of optimal porosities after compression.

Acknowledgments

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References

- [1] S. Pejovnik, R. Dominko, M. Bele, M. Gaberscek, J. Jamnik, J. Power Sources 184 (2008) 593.
- [2] F.M. Courtel, S. Niketic, D. Duguay, Y. Abu-Lebdeh, I.J. Davidson, J. Power Sources 196 (2011) 2128.
- [3] J. Li, C. Daniel, D. Wood, J. Power Sources 196 (2011) 2452.
- [4] M. Gaberscek, M. Bele, J. Drogenik, R. Dominko, S. Pejovnik, Electrochem. Solid-State Lett. 3 (2000) 171.
- [5] R. Dominko, M. Gaberscek, J. Drogenik, M. bele, S. Pejovnik, Electrochem. Solid-State Lett. 4 (2001) A187.

- [6] W. Porcher, B. Lestriez, S. Jouanneau, D. Guyomard, J. Electrochem. Soc. 156 (2009) A133.
- [7] W. Porcher, B. Lestriez, S. Jouanneau, D. Guyomard, J. Power Sources 195 (2010) 2835.
- [8] J.H. Lee, U. Paik, V.A. Hackley, Y.M. Choi, J. Electrochem. Soc. 152 (2005) 1763.
- [9] W.R. Liu, M.H. Yang, H.C. Wu, S.M. Chiao, N.L. Wu, Electrochem. Solid-State Lett. 8 (2005) 100.
- [10] H. Buqa, M. Holzapfel, F. Krumeich, C. Veit, P. Novák, J. Power Sources 161 (2006) 617.
- [11] J.H. Lee, Y.M. Choi, U. Paik, J.G. Park, J. Electroceram 17 (2006) 657.
- [12] J.H. Lee, S. Lee, U. Paik, Y.M. Choi, J. Power Sources 147 (2005) 249.
- [13] S.F. Lux, F. Schappacher, A. Balducci, S. Passerini, M. Winter, J. Electrochem. Soc. 157 (2010) A320.
- [14] A. Guerfi, M. Kaneko, M. Petitclerc, M. Mori, K. Zaghib, J. Power Sources 163 (2007) 1047.
- [15] C.C. Li, J.T. Lee, Y.L. Tung, J. Mater. Sci. 42 (2006) 5773.
- [16] J.T. Lee, Y.J. Chu, F.M. Wang, C.R. Yang, C.C. Li, J. Mater. Sci. 42 (2007) 10118.
- [17] C.C. Li, X.W. Peng, J.T. Lee, F.M. Wang, J. Electrochem. Soc. 157 (2010) A517.
- [18] K. Zaghib, M. Dontigny, A. Guerfi, P. Charest, I. Rodrigues, A. Mauger, C.M. Julien, J. Power Sources 196 (2011) 3949.
- [19] P. Zuo, W. Yang, X. Cheng, G. Yin, Ionics 17 (2011) 87.
- [20] J.H. Lee, J.S. Kim, Y.C. Kim, D.S. Zang, Y.M. Choi, W. Il Park, U. Paik, Electrochem. Solid-State Lett. 11 (2008) A175.
- [21] C.C. Li, Y.W. Wang, J. Electrochem. Soc. 158 (2011) A1361.
- [22] C. Fongy, A.C. Gaillot, S. Jouanneau, D. Guyomard, B. Lestriez, J. Electrochem. Soc. 157 (2010) A885.